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TITLE OF INVENTIONLIGNIN BASED COLLOIDAL COMPOSITIONSFIELD OF INVENTION

721  
5 The present invention relates to the processing of black liquor and the preparation of bitumen compositions containing black liquor.

BACKGROUND TO THE INVENTION

10 Black liquor is an aqueous alkaline pulping residue produced in Kraft pulping of wood chips in a pulp mill to provide wood fibers for paper-making. Black liquor generally contains about 55 to 65% solids comprising lignin, sodium salts of poly-saccharinic acids, organic and inorganic sulfides and carbonates and many other compounds. The lignin in the black liquor is the main  
15 organic component and is present as a high mass colloid stabilized by ionized phenolic groups. Lignin is a phenylpropane polymer of amorphous structure comprising about 17 to about 30% of wood. Lignin is so closely associated with the cellulosic fibres and hemicellulose that makes up the balance of woody material that lignin  
20 can be separated from wood only by chemical reaction at high temperature, such as that used in the Kraft pulping process, wherein wood chips are digested with an aqueous alkaline solution of sodium hydroxide and hydrogen sulfide, known as white liquor. Normally, the black  
25 liquor, after separation of the wood fibers, is processed to remove organic materials and to recover and regenerate pulping chemicals. Lignin can be recovered from wood-processing wastes only in limited quantities.

30 The lignin is a natural binder derivative of wood. Alkali lignin from both softwoods and hardwoods are useful in many products. They are used as stabilizers for asphalt emulsions, modifiers and extenders for latex emulsions, compounding agents in vinyl plastics, soil  
35 conditioners, binders in printing inks, wood stains, protective colloids in soap emulsions, dispersing agents

for clay, fire foam stabilizers, drilling mud additives, insecticide dispersants, absorbers in storage batteries and foundry sand binders. Alkali lignin can also be used as adhesives for plywood, molding powders and formed  
5 insulating resins and as a reinforcing agent for rubber.

Asphalt binders (or bitumen) are widely used in different applications, such as asphalt-aggregate blends for road paving, asphalt fiber reinforced membranes for roofing and asphalt-water emulsions in surface treating  
10 both for paving and roofing. Problems for straight-run asphalt in those applications are the tendency to become brittle at low temperatures and to become soft at high temperatures, the tendency to flow under constant load at service temperatures and the tendency to phase  
15 separation during storage when mixed with other components.

Various approaches have been used for the purpose of improving asphalt compositions to address these problems. For instance, polymers have been utilized to  
20 improve the high and low temperature characteristics of asphalt compositions, as well as to improve their toughness and durability. Air blowing of straight-run asphalt has been used to improve stiffness and dimensional stability for hot applied roofing systems.  
25 The asphalt may be treated with acid to improve its compatibility with the polymeric additives. Lignin or lignin based additives have been widely used to emulsify asphalt to achieve a stable dispersion of asphalt in aqueous medium.

30 Black liquor is an aqueous colloidal system in which ample lignin is present. However, means have not been previously disclosed whereby a stable dispersion of lignin in asphalt can be achieved by combining black liquor with hot liquid asphalt. When the black liquor is  
35 added to the bitumen and dispersed with agitation into molten asphalt cement, de-watering of the black liquor

occurs while lignin and other salts in the black liquor tend to form large, rigid aggregates which separate from the liquid asphalt and subsequently strongly resist dispersion in the asphalt.

5 It is one objective of the present invention to develop a process or processes whereby liquor-solid pulping residue (black liquor) can be converted from one in which water is the dispersing and plasticizing agent to one in which water is replaced by oil, achieving a  
10 dispersion in which a lignin based colloidal particulate phase is stably maintained. It is another objective to provide a lignin-oil dispersion which can be smoothly blended with liquid asphalt to produce a stable, homogeneous dispersion.

15 SUMMARY OF INVENTION

The present invention relates to compositions and methods for combining black liquor with selected petroleum-derived products. More specifically, this invention provides two separate processes for preparing lignin-based colloidal dispersions in lubricating or other petroleum-based oils. The lignin-oil colloidal dispersions prepared by either of such processes may be blended with bitumen to produce novel bituminous composition. Two embodiments of such procedures are described herein. The black liquor used in the invention may be that resulting from cooking wood in an alkaline solution in the soda or sulfate (Kraft) paper-making process.

The asphalt employed in this invention can be any of the well known bituminous substances derived from petroleum, shale oil, coal tar and the like. Commonly, the asphalt is prepared by vacuum distillation of a topped crude oil. Preferably, the asphalt has a penetration at 25°C (as determined by ASTM D5) ranging for about 20 to about 400.

In a first embodiment of the invention, the

procedure involves essentially two steps. In the first step, the black liquor is converted from its aqueous colloidal system to an anhydrous colloidal dispersion in a lubricating oil medium in which a surfactant, which  
5 may be an anionic surfactant, such as DDBSA (dodecylbenzene sulfuric acid), is used to promote the provision of the anhydrous colloidal dispersion. The process may be effected under low shear conditions.

10 The anhydrous colloidal dispersion of lignin in oil may be mixed, in a second step, with asphalt bitumen, producing a unique combination, which is a novel bituminous composition.

15 In another embodiment of the invention, the procedure again involves essentially two steps. First, bitumen is treated with an inorganic acid, such as sulfuric acid, at elevated temperature to provide an acid-treated bitumen. The black alkaline liquor is then added slowly to the acid-treated bitumen under agitation for de-watering the black liquor at a controlled rate to  
20 form a stable, substantially anhydrous, colloidal dispersion of lignin in the bitumen, also to provide a novel bituminous composition.

Accordingly, in another aspect of the present invention, there is provided a bituminous composition  
25 comprising bitumen, and dewatered lignin-containing spent alkaline pulping liquor dispersed therein. The dewatered spent alkaline pulping liquor may be present in an amount up to about 50 wt.% of the bitumen, preferably about 5 to about 25 wt.% of the bitumen.

30 In such composition, the dewatered spent alkaline pulping liquor may comprise an anhydrous colloidal dispersion of lignin in a lubricating oil. The dewatered spent alkaline pulping liquor may comprise a stable, substantially anhydrous, colloidal dispersion of  
35 lignin in the bitumen.

DETAILED DESCRIPTION OF THE INVENTION

Referring first to the first embodiment of the invention, a lubricating oil is mixed with black liquor at temperatures below the water boiling point. A  
5 surfactant, which may be DDBSA (dodecylbenzene sulfuric acid), is selected to be added to the mixture to facilitate the colloidal dispersion of black liquor in the lubricating oil while de-watering is gradually carried out at an elevated temperature. The dewatering  
10 may be effected by starting at an elevated temperature, which may be about 100° to about 180°C, preferably about 110° to about 160°C. The resulting cream-like paste product is miscible with hot liquid asphalt at any ratio to form a novel bituminous composition.

15 The lubricating oil used in the first embodiment of the invention may be a re-refined waste motor oil or other convenient petroleum-based oil. Contaminants of waste motor oil, such as dirt, lead, arsenic and other harmful metals and chemicals, are removed from the waste  
20 motor oil to produce a clean base lubricating oil by the re-refining process.

The lubricating oil may be a selected fraction of refined mineral oil used for lubrication of moving surfaces. Such fraction may range in consistency from  
25 thin liquid to grease-like substances. Usually, lubricating oils contain small amounts of additives to impart special properties, such as viscosity index and detergency.

The surfactant or dispersing agent used in the  
30 process may typically be dodecylbenzene sulfuric acid (DDBSA), although other anionic surfactants may be employed, if desired, such as fatty acid, linear alkyl sulfonates having 10 or more carbon atoms in the chain. DDBSA is benzene with dodecene, and the resulting  
35 dodecylbenzene is sulfonated. DDBSA may be neutralized with caustic soda from the alkaline black liquor or

other convenient source to promote the detergency of the lubricating oil and to reduce surface tension in the mixture.

5 However, a surfactant need not always be necessary, if the lubricating oil employed has a detergency high enough to ensure that a colloidal dispersion of the solid residue from the black liquor is achieved in the lubricating oil medium.

10 The lignin-oil dispersion produced by either of these procedures may be smoothly blended with bitumen to provide the desired lignin-asphalt composition. The spent pulping liquor, which may be black liquor from a kraft pulp mill, may be present in an amount of about 25 to about 60 wt.% of the composition, preferably about 25 to 40 wt.% of the composition.

15 Referring now to the second embodiment of the invention, the bitumen first is treated with a strong mineral acid, such as sulfuric acid, at elevated temperature and then the alkaline black liquor is added to the treated bitumen at a controlled rate under agitation to effect de-watering of the black liquor to form a stable, substantially anhydrous, colloidal dispersion in the bitumen. The elevated temperature may be about 100° to about 180°C, preferably about 110° to about 160°C. The spent pulping liquor may be present in an amount of about 5 to about 50 wt.% of the composition, preferably about 10 to about 30 wt.%

20 An inorganic acid is contacted with, or added to, the asphalt to form an acid treated asphalt. In general, the acid addition shifts the asphalt structure from a sol to a gel, lowers the temperature susceptibility of the asphalt and improves the stability of the additive dispersion in the treated asphalt. Since black liquor is an aqueous alkaline system, it is critical that the acid not be added to the asphalt after addition of or with the black liquor.

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Preferably, the acid is added slowly to the asphalt to avoid foaming, which may occur if all the acid were added at one time. The inorganic acid content of the asphalt resulting from the acid treatment is not  
5 critical, but normally is in the range between about 0.2 and about 3.5 wt%, preferably between about 0.5 and about 2.5 wt% of the asphalt. Although a wide variety of inorganic acids can be used for treatment of the asphalt, the inorganic acid is preferably selected from  
10 the group consisting of sulfuric acid, phosphoric acid, poly-phosphoric acid, phosphorous pentoxide, hydrochloric acid, and mixtures thereof. The sulfuric acid, phosphoric acid or poly-phosphoric acid are preferred inorganic acids, with the sulfuric acid being  
15 particularly preferred.

Following acid addition, the alkaline black liquor is then added slowly to the acid-treated bitumen at an elevated temperature, typically around 100°C, under agitation for a certain period of time to permit de-  
20 watering of the black liquor to occur while the solids are incorporated into the bitumen. The temperature of the final composition next is increased above the boiling point of water, typically up to around 160°C until residual water is completely evaporated off to

form a stable, substantially anhydrous, colloidal lignin dispersion in the bitumen.

### EXAMPLES

#### Example 1:

5           This Example illustrates the first embodiment of the invention in which black liquor first dispersed in a lubricating oil and then in bitumen.

#### General Procedure:

10           Black liquor and DDBSA were mixed at room temperature in specific proportions under stirring for 20 to 30 min to form a mixture. Re-refined waste lube oil was added into the mixture at room temperature to a desired concentration and stirred another about 20 min. The resulting mixture was heated slowly to about 160° to 15           180°C for about 2 to 3 hours under stirring until water-free. During this step, the viscosity of the system exhibited complex phenomena because a raising of the temperature resulted in reduced viscosity while water loss resulted in increased viscosity. Accordingly, the 20           temperature and time for de-watering must be controlled.

#### Specific Experiments:

25           16 Kg of DDBSA was added to 266 g of black liquor (ca. 60% solid content) and stirred at room temperature for 20 to 30 min. 184 g of reclaimed lube oil were added and stirred again at room temperature for 20 to 30 min. The temperature of the mixture was slowly raised from room temperature to 170°C for 2 to 3 hours to de-water the composition. After de-watering and cooling, about 332 g sample was obtained. The sample was a black 30           colored paste and water-free and was easily dispersed into asphalt at any ratio. This sample was designated as B-14, seen in Table 1.

35           Different black liquor/lube oil formulations have been prepared following the above procedure and the data are presented in the following Table 1:



TABLE 1  
NON-AQUEOUS DISPERSING SYSTEM OF BLACK LIQUOR/LUBE OIL

Sample Code	Black liquor g	DDBSA		Lube Oil		Product Wt. g
		g	wt%	g	wt%	
B-13	246	24	4.6	254	48.5	410
B-14	266	16	3.4	184	39.5	332
B-15	218	6.0	1.94	180	44.6	302
B-19	336	10	2.15	120	25.8	308
B-20	460	14	2.35	122	20.5	372
PR-30	590 (1 part)	17.7 (0.03 part)		413 (0.7 part)		

Note: Mass of analyzed sample of reclaimed lube oil (recovered from engine oil) was determined following the test method of ASTM 4124-92.

Base asphalt (or bitumen) used in the present invention were selected from three different grades: AC-5 having an absolute viscosity of around 500 poises, I85/100 having a 25°C penetration range from 65 dmm to 100 dmm and I120/150 having a 25°C penetration range from 120 dmm to 150 dmm. The non-aqueous dispersing system of black liquor/lube-oil produced as described in the Table 1 was dispersed into hot liquid asphalt at about 160°C respectively to form a very fine dispersion mixture. The stability of these lignin based bituminous mixtures during hot storage at elevated temperature was evaluated using a conditioned tube test. The conditioning procedure consists of placing approximately 70g of the mixture in ¾" aluminum tubes and storing such tubes in a vertical position at 165°C in an oven for 48 hrs. Following hot storage, a viscosity ratio was determined by comparing the viscosity of the mixture tested at 135°C from the bottom section of the sample and from the top section of the sample in the tube. A ratio in the range of 0.80 to 1.20 is generally considered acceptable with respect to separation of the dispersed phase. The testing results on eight compositions are shown in the following Table 2. The results indicate that the lignin based solid dispersion in asphalt binder are quite stable.

TABLE 2  
STABILITY OF THE BLACK LIQUOR/LUBE OIL BLEND (BLB) IN HOT ASPHALT

Code	Asphalt		BLB			Viscosity, cp at 135°C	Stability Index*
	Name	(g)	Code	(g)	(%)		
AB5-16	AC5	368	B-13	38	10	455/463	0.98
B14-85-10	I85/160	90	B-14	10	10	387.5/432.5	0.90
B14-85-20	I85/160	80	B-14	20	20	450/465	0.97
B14-85-30	I85/160	70	B-14	30	30	435/500	0.87
B15-A	II20/150	70	B-15	30	30	825/845	0.97
B15-B	II20/150	85	B-15	15	15	257/265	0.97
B20-20	II20/150	80	B-20	20	20	740/802.5	0.97
RB30-30	II20/150	80	PP-30	20	20	405/475	0.85

Note: (1) In the better formulations of the non-aqueous dispersing system, an appropriate composition was a lube oil content of more than 20% and DBSA content of greater than 2%.

(2) DBSA is dodecylbenzene sulfonic acid.

$$\text{Stability Index} = \frac{\text{Viscosity at top}}{\text{Viscosity at bottom}}$$

Example 2:

This Example illustrates the second embodiment of the invention in which bitumen first is acidified.

General Procedure:

5 Sulfuric acid (95 to 98%  $H_2SO_4$ ) was added into hot asphalt AC-5 at 100° to 110°C under stirring (800 to 1000 RPM) for 20 to 30 mins. to form an acid-modified asphalt, followed by addition of aqueous black liquor (c.a. 60% solid content) into the acid-modified asphalt,  
10 according to the following procedure.

- (1) While stirring at 800 to 1000 RPM, the acid was added into asphalt at 100° to 110°C for 20 to 30 min. and acid-modified asphalt was obtained.
- (2) After 20 to 30 min., black liquor was added to the  
15 acid-modified asphalt at 105° to 115°C for 30 to 40 min., then maintained for 1 to 2 hours for dewatering.
- (3) The temperature was slowly increased to 170°C while stirring for 1 to 2 hours to effect further  
20 dewatering.
- (4) The composition was allowed to cool and was sampled for stability.

Specific Experiments:

To 392 g of asphalt AC-5 were added 3.14 g of  $H_2SO_4$   
25 (0.8% AC-5) at 100° to 110°C under 800 to 1000 RPM stirring for 20 min. The acidified asphalt was maintained at 100° to 110°C and black liquor 84 g (22% AC-5) was added over about 30 min., and then the composition was maintained for 1 to 2 hrs at 105° to  
30 115°C to dewater the black liquor. The temperature was raised to 170°C while stirring to effect further dewatering. The product was then cooled to provide 436 g of product (loss mass 43 g). The stability index determined on this sample (AC-B-18) was 0.94, shown in  
35 Table 3.

Results of dispersion and stability determinations are also shown below in the following Table 3. The results shown in Table 3 indicate that products of formulation containing 0.8 wt% acid and 0 to 30 wt%, preferably 15 to 25 wt% black liquor, based on the amount of asphalt, had good stability.

TABLE 3  
EXPERIMENTAL FORMULATIONS AND STABILITY

Code	Asphalt (AC-5)	Acid		Black Liquor		Viscosity cp after 48 hrs storage at 160°C		
		(g)	(%)	(g)	(%)	Top	Bottom	Stability Index
AC-B-24	374	0	0	112	30	Sediment appeared <sup>(1)</sup>		
AC-B-11	472	2.4	0.5	94	20	413	550	0.75
AC-B-10	362	4.0	1.1	72	20	298	310	0.96
AC-B-18	392	3.14	0.8	84	22	338	358	0.94
AC-B-25	294	2.35	0.8	59	20	312.5	317.5	0.98
AC-B-26	388	2.3	0.8	72	25	360	342.5	1.05
AC-B-19	360	2.94	0.8	110	30	270	598	0.45
AC-B-23	380	3.8	1.0	114	30	290	907.5	0.32
AC-B-21	360	4.32	1.2	108	30	377.5	360	1.05
AC-B-22	373	3.73	1.0	149	40	300	402.5	0.75
AC-B-20	380	3.0	0.8	190	50	267.5	1060	0.25

Note: (1) No measurement was possible.

SUMMARY OF THE DISCLOSURE

In summary of this disclosure, the present invention provides novel procedures for the stable dispersion of lignin components of black liquor in bitumen. Modifications are possible within the scope of the invention.